

STATISTICAL DERIVATION OF BASIC EQUATIONS OF DIFFUSIONAL KINETICS IN ALLOYS WITH APPLICATION TO THE DESCRIPTION OF DIFFUSION OF CARBON IN AUSTENITE

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Basic equations of diffusional kinetics in alloys are statistically derived using the master equation approach. To describe diffusional transformations in substitution alloys, we derive the "quasi-equilibrium" kinetic equation which generalizes its earlier versions by taking into account possible "interaction renormalization" effects. For the interstitial alloys Me-X, we derive the explicit expression for the diffusivity D of an interstitial atom X which notably differs from those used in previous phenomenological treatments. This microscopic expression for D is applied to describe the diffusion of carbon in austenite basing on some simple models of carbon-carbon interaction. The results obtained enable us to make certain conclusions about the real form of these interactions, and about the scale of the "transition state entropy" for diffusion of carbon in austenite.

1 INTRODUCTION

The problem of development of an adequate theoretical description of diffusion in alloys attracts interest from both fundamental and applied standpoints, see, e. g. [1]-[15]. Presently, this description is usually based on the phenomenological theory of diffusion in multicomponent systems developed by Onsager many years ago [6]. Phenomenological kinetic coefficients of this theory are calculated using various simplified models with parameters estimated empirically [1]-[4]. However, these empirical models have usually no consistent theoretical justification, and their relation to interatomic interactions, as well as possibilities of applications to other alloy systems, are typically not clear.

One of important problems in this field is the strong concentration dependence of the diffusivity D of carbon in austenite [1]-[5]. This dependence causes complications in the kinetic analysis of various diffusion-controlled reactions in steels [4], and several empirical models have been suggested to describe this dependence [1]-[4]. However, possibilities to

employ these models for predictions of D at temperatures $T \lesssim 1000$ K (where many important phase transformations occur but D can not be directly measured as austenite is unstable here) or under partial substitution of iron by other metals are, generally, not clear [5].

The consistent statistical description of the diffusional kinetics in alloys can be based on the master equation approach [7]-[15]. This approach enables us to express the phenomenological kinetic coefficients, such as the mobility M_α of an α -species atom, via interatomic interactions in an alloy. These interactions can be estimated using either some microscopic models [16]-[18] or *ab-initio* methods [14, 19, 20]. As the level of accuracy and reliability of *ab-initio* calculations is steadily increasing, this microscopic approach seems to be prospective for non-empirical calculations of diffusivity.

At the same time, previous considerations of diffusional kinetics in alloys based on the master equation approach were usually restricted by discussions of only simplest models and approximations or some particular problems [7, 8, 9, 11, 13]. On the other hand, few more general discussions [10, 15] included many not necessary complications and restrictions which can hinder the understanding of the results. Therefore, the first aim of this paper is to present a clear and general derivation of basic equations of diffusion in alloys based on the master equation approach, for both substitution and interstitial alloys.

To this end, in Sec. 2 we first discuss the vacancy-mediated kinetics under diffusional transformations in substitution alloys. This problem has been considered in Ref. [15], and some equations derived in Sec. 2 have been already presented there. However, the full derivation of these equations has not been given in [15], while the similar derivation in [10] includes a number of complications and inaccuracies. In Sec. 2 we also discuss the methods of computer simulations based on the microscopic equations proposed, including some generalizations of the earlier-discussed “equivalence theorem” [10, 15] which greatly simplifies such simulations. In Sec. 3 we consider the interstitial alloys Me-X and derive the general statistical expression for the diffusivity D of an interstitial atom X which has a simple and physically transparent form. This expression includes only microscopic parameters which can be estimated using either theoretical models or *ab-initio* calculations. We also generalize this microscopic expression for D for the case of multicomponent alloys (Me₁Me₂...)-X with several species atoms in the metal sublattice.

The second aim of this work is to apply the results of Sec. 3 to microscopically treat the above-mentioned problem of diffusion of carbon in austenite. This treatment described in Sec. 4 is based on the microscopic model of carbon-carbon (C-C) interactions in austenite suggested by Blanter [16] which supposes a strong “chemical” repulsion at short C-C distances R_{CC} and a purely deformational (or “strain-induced”) interaction at longer distances R_{CC} . We show that some natural generalizations of this model enable us to describe both thermodynamic and diffusional characteristics of carbon in austenite at the same level of accuracy as that achieved in phenomenological models [1, 2, 3, 4, 36]. At the same time, the microscopic approach used enables us to make a number of conclusions about the type of carbon-carbon interactions and about some physical features of diffusion of carbon in austenite. The main results of this work are summarized in Sec. 5.

2 EQUATIONS OF VACANCY-MEDIATED KINETICS FOR DIFFUSIONAL TRANSFORMATIONS IN SUBSTITUTION ALLOYS

2.1 General equations for mean occupations of lattice sites

First we present the necessary relations from Ref. [15] with some extensions and comments. We consider a substitutional alloy with $(m+1)$ components p' that includes atoms of m different species $p = p_1, p_2, \dots, p_m$ and vacancies v : $p' = \{p, v\}$. The distributions of atoms over the lattice sites i are described by the different occupation number sets $\{n_i^{p'}\}$ where the operator $n_i^{p'}$ is 1 when the site i is occupied by a p' -species component and 0 otherwise. For each i these operators obey the identity $\sum_{p'} n_i^{p'} = 1$, so only m of them are independent. It is convenient to mark the independent operators with Greek letters ρ or σ : $(n_i^{p'})_{indep} = n_i^\rho$, while the rest operator denoted as n_i^h is expressed via n_i^ρ :

$$n_i^h = \left(1 - \sum_{\rho} n_i^\rho\right). \quad (1)$$

Note that both n_i^h and n_i^ρ are the projection operators:

$$(n_i^h)^2 = n_i^h, \quad n_i^h n_i^\rho = 0, \quad n_i^\rho n_i^\sigma = \delta_{\rho\sigma} n_i^\rho. \quad (2)$$

For dilute alloys, it is convenient to put “ h ” in (1) to be the host component, e.g., $h = \text{Fe}$ for the dilute BCC Fe-Cu- v alloys discussed in [14, 15] and used below for illustrations.

In terms of all operators $n_i^{p'}$ the total configurational Hamiltonian H^t (for simplicity supposed to be pairwise) can be written as

$$H^t = \frac{1}{2} \sum_{p'q', ij} V_{ij}^{p'q'} n_i^{p'} n_j^{q'}. \quad (3)$$

After elimination of the operators n_i^h according to (1), this Hamiltonian takes the form

$$H^t = E_0 + \sum_{\rho i} \varphi_\rho n_i^\rho + H_{int}, \quad H_{int} = \sum_{\rho\sigma, i>j} v_{ij}^{\rho\sigma} n_i^\rho n_j^\sigma \quad (4)$$

which includes only independent n_i^ρ , while constants E_0 , φ_ρ , and “configurational interactions” $v_{ij}^{\rho\sigma}$ are linearly expressed in terms of the couplings $V_{ij}^{p'q'}$ in (3), in particular:

$$v_{il}^{\rho\sigma} = (V^{\rho\sigma} - V^{\rho h} - V^{h\sigma} + V^{hh})_{ij}. \quad (5)$$

The fundamental master equation for the probability P of finding an occupation number set $\{n_i^\rho\} = \xi$ is [12]:

$$dP(\xi)/dt = \sum_{\eta} [W(\xi, \eta)P(\eta) - W(\eta, \xi)P(\xi)] \equiv \hat{S}P \quad (6)$$

where $W(\xi, \eta)$ is the $\eta \rightarrow \xi$ transition probability per unit time. If we adopt for probabilities W the conventional “transition state” model [14], we can express the transfer matrix \hat{S} in (6) in terms of the probability of an elementary inter-site exchange (“jump”) $pi \rightleftharpoons vj$ between neighboring sites i and j :

$$W_{ij}^{pv} = n_i^p n_j^v \omega_{pv}^{eff} \exp[-\beta(\hat{E}_{pi,vj}^{SP} - \hat{E}_{pi,vj}^{in})] \quad (7)$$

where $\beta = 1/T$ is the reciprocal temperature, $\hat{E}_{pi,vj}^{SP}$ is the saddle point energy, $\hat{E}_{pi,vj}^{in}$ is the initial (before the jump) configurational energy of a jumping atom p and a vacancy, and the pre-exponential factor ω_{pv}^{eff} can be written as

$$\omega_{pv}^{eff} = \omega_{pv} \exp(\Delta S_{pi,vj}^{SP}). \quad (8)$$

Here ω_{pv} is the attempt frequency which, generally, is expected to have the order of magnitude of a mean frequency of vibrations of a jumping atom in an alloy, and $\Delta S_{pi,vj}^{SP}$ is the entropy difference between the saddle-point and the initial alloy states. This difference is mainly due the difference of atomic vibrations in the saddle-point state (supposed to be locally equilibrium so that such thermodynamic notion as the entropy can be applied to it) and the initial state. At high temperatures T under considerations (actually, already at $T \gtrsim \theta/2$ where θ_D is the Debye temperature [22]), this entropy difference can be described by the classical expression:

$$\Delta S_{pv}^{SP} = 3 \ln(\bar{\omega}_p^{in}/\bar{\omega}_p^{sp}) \quad (9)$$

where $\bar{\omega}_p^{in}$ and $\bar{\omega}_p^{sp}$ are certain average frequencies of vibrations of a jumping atom in the initial and in the saddle point states, respectively, see, e. g., [29]. As frequencies ω_p^{sp} in the saddle-point configuration can notably soften with respect to ω_p^{in} , the entropy difference ΔS_{pv}^{SP} can be expected to take significant positive values. For example, for the Fe-Cu- v alloys with the Debye frequency $\omega_D^{\text{Fe}} \simeq 6 \cdot 10^{13} \text{ sec}^{-1}$ [23], Soisson and Fu (SF) [14] found: $\omega_{\text{Fe}v}^{eff} \sim 80 \omega_D^{\text{Fe}}$, $\omega_{\text{Cu}v}^{eff} \sim 30 \omega_D^{\text{Fe}}$. It implies: $\Delta S_{\text{Fe}v}^{SP} \sim 4.5$, $\Delta S_{\text{Cu}v}^{SP} \sim 3.5$, $\bar{\omega}_{\text{Fe}}^{sp} \sim \omega_D^{\text{Fe}}/4$, $\bar{\omega}_{\text{Cu}}^{sp} \sim \omega_D^{\text{Fe}}/3$, though so high values of ΔS^{SP} and $\omega_D/\bar{\omega}^{sp}$ can be somewhat overestimated due to inaccuracies of estimates [14].

The saddle point energy $\hat{E}_{pi,vj}^{SP}$, generally, depends on the atomic configuration near the ij bond. We describe this dependence by the model of SF [14] supposing the saddle-point energy to depend only on occupations of lattice sites l nearest to the center of bond ij (denoted by l_{nn}^{ij}):

$$\hat{E}_{pi,vj}^{SP} = \sum_{q, l=l_{nn}^{ij}} \varepsilon_q^p n_l^q = E_h^p + \hat{\Delta}_{ij}^p. \quad (10)$$

Here E_h^p is the saddle point energy for the pure host metal, while the operator $\hat{\Delta}_{ij}^p$ describes changes in this energy due to a possible presence of minority atoms near the bond:

$$E_h^p = z_{nn}^b \varepsilon_h^p; \quad \hat{\Delta}_{ij}^p = \sum_{\rho, l=l_{nn}^{ij}} \Delta_{\rho}^p n_l^{\rho} \quad (11)$$

where z_{nn}^b is the total number of nearest lattice sites l for each bond (being $z_{nn}^b = 6$ for the BCC lattice), $\Delta_{\rho}^p = (\varepsilon_{\rho}^p - \varepsilon_h^p)$, while $(\varepsilon_{\rho}^p$ and $\varepsilon_h^p)$ are the microscopic parameters of pairwise interactions calculated by SF using *ab-initio* methods [14]. Note that our definitions of $\hat{\Delta}_{ij}^p$ and Δ_{ρ}^p differ by sign from those used in [14] and [15].

The interaction parameters $V_{ij}^{p'q'}$, ε_h^p and Δ_{ρ}^p in Eqs. (3) and (11) can be calculated by *ab-initio* methods. For the Fe-Cu- v alloys it is illustrated by SF [14]. Theoretical calculations of factors ω_{pv}^{eff} in Eq. (7) are more difficult due to the presence of the entropic factor $\exp(\Delta S_{pv}^{SP})$ in Eq. (8). However, values of ω_{pv}^{eff} can be estimated from experimental data about the self-diffusion and the diffusion of isolated atoms in a host metal, as described by SF [14].

As n_i^{ρ} in Eqs. (1), (4), and (6) are the projection operators obeying Eqs. (2), the most general expression for the probability $P = P\{n_i^{\rho}\}$ in (6) can be written in the form of

the generalized Gibbs distribution [10, 11, 12]

$$P\{n_i^\rho\} = \exp \left[\beta \left(\Omega + \sum_{\rho i} \lambda_i^\rho n_i^\rho - H_{int} - \hat{h}_{int} \right) \right], \quad (12)$$

$$\hat{h}_{int} = \frac{1}{2} \sum_{\rho\sigma, ij} h_{ij}^{\rho\sigma} n_i^\rho n_j^\sigma + \frac{1}{6} \sum_{\rho\sigma\tau, ijk} h_{ijk}^{\rho\sigma\tau} n_i^\rho n_j^\sigma n_k^\tau + \dots \quad (13)$$

Here parameters λ_i^ρ (which are both time- and space-dependent, in general) can be called “site chemical potentials” for ρ -species atoms; they are related to local chemical potentials μ_i^ρ and μ_i^h of ρ -species and host atoms as $\lambda_i^\rho = (\mu_i^\rho - \mu_i^h)$ [21]. H_{int} in (12) is the same as in (4); the parameters $h_{i\dots j}^{\rho\dots\sigma}$ in (13) (also depending on both time and space) describe possible renormalizations of interactions; and Ω is determined by normalization.

As discussed in detail in [12], for the usual conditions of phase transformations corresponding to the absence of external fluxes of particles or energy (that is, when the alloy is a “closed” but not an “open” statistical system), the effects of renormalizations of interactions can be expected to be insignificant, thus one can put in (12):

$$\hat{h}_{int} = 0. \quad (14)$$

There are at least two reasons to expect the validity of Eq. (14) for the transformations in closed systems. First, this relation holds both before and after the transformation. For example, it is true before an initially equilibrated alloy is quenched from a higher temperature T_h to the lower temperature T_l corresponding to another equilibrium phase (or phases), and it is also true after the new equilibrium state at $T = T_l$ is reached. Therefore, there is no driving force drawing the correlation parameters $h_{i\dots j}^{\rho\dots\sigma}$ in the distribution (12) away from their Gibbs values $h_{i\dots j}^{\rho\dots\sigma} = 0$. Second, the parameters $h_{i\dots j}^{\rho\dots\sigma}$ in the distribution (12) describe mainly the short-range order. After a change of external conditions, such as temperature, this short-range order is established relatively fast, for a time of the order of one interatomic exchange time τ_a , while the time for completing microstructural evolution under phase transformation is usually much longer: $t \gg \tau_a$ [8, 10, 15]. Therefore, possible fluctuative violations of relation (14) at small $t \lesssim \tau_a$ are not important for the whole evolution.

When relation (14) is obeyed, Eq. (12) takes the form:

$$P\{n_i^\rho\} = \exp \left[\beta \left(\Omega + \sum_{\rho i} \lambda_i^\rho n_i^\rho - H_{int} \right) \right] \quad (15)$$

which will be called the “quasi-equilibrium Gibbs distribution”.

Note, however, that for the essentially “open” systems, such as alloys under irradiation [24, 25] or an alloy with an external atomic flux imposed [11], the quasi-equilibrium relation (14) can be significantly violated. Important cases of such violations can be the phase transformations accompanied by significant fluxes of vacancies into the transformation region, for example, the precipitation in Fe-Cu-*v* alloys where these fluxes arise due to the strong trapping of vacancies by the copper-based precipitates [14]. In such cases, the effective vacancy-copper interactions can notably vary with the evolution time, and the presence of significant renormalizations $h_{ij}^{vCu} \neq 0$ can be expected. Possible methods of calculations of these renormalizations have been discussed in [10, 11, 13].

Multiplying Eq. (6) by operators n_i^ρ and summing over all configurations $\{n_i^\sigma\}$, we obtain the set of equations for mean occupations of sites (“local concentrations”) $c_i^\rho = \langle n_i^\rho \rangle$:

$$dc_i^\rho/dt = \langle n_i^\rho \hat{S} \rangle \quad (16)$$

where $\langle(\dots)\rangle = \sum_{\{n_j^\sigma\}}(\dots)P\{n_j^\sigma\}$ means averaging over the distribution P , for example:

$$c_i^\rho = \langle n_i^\rho \rangle = \sum_{\{n_j^\sigma\}} n_i^\rho P\{n_j^\sigma\}. \quad (17)$$

For what follows it is convenient to mark the minority atoms by Greek indices α, β, \dots . Then index p in Eqs. (7)-(12) is α or h , corresponding to a minority or a host atom, while index ρ in Eqs. (12)-(16) is α or v , corresponding to a minority atom or a vacancy. Then the system of equations (16) can be explicitly written as follows:

$$\begin{aligned} \frac{dc_i^\alpha}{dt} &= \sum_{\{n_k^\rho\}} \sum_{j(i)} \omega_{\alpha v}^{eff} \left[n_i^\alpha n_j^\alpha \exp(\beta \hat{E}_{\alpha i, v j}^{in} - \beta \hat{E}_{\alpha i, v j}^{SP}) - \{i \rightarrow j\} \right] \exp[\beta(\Omega - H_{eff})] \\ \frac{dc_i^v}{dt} &= \sum_{\{n_k^\rho\}} \sum_p \sum_{j(i)} \omega_{pv}^{eff} \left[n_i^p n_j^v \exp(\beta \hat{E}_{pi, v j}^{in} - \beta \hat{E}_{pi, v j}^{SP}) - \{i \rightarrow j\} \right] \exp[\beta(\Omega - H_{eff})] \end{aligned} \quad (18)$$

where symbol $j(i)$ means summation over sites j being nearest neighbors of site i , and p is h or α , while $H_{eff} = H_{eff}\{n_k^\rho\}$ is the effective Hamiltonian for statistical averaging of expressions in square brackets:

$$H_{eff} = - \sum_{\rho, k} \lambda_k^\rho n_k^\rho + \frac{1}{2} \sum_{\rho\sigma, kl} \tilde{v}_{kl}^{\rho\sigma} n_k^\rho n_l^\sigma, \quad \tilde{v}_{kl}^{\rho\sigma} = (v_{kl}^{\rho\sigma} + h_{kl}^{\rho\sigma}). \quad (19)$$

Here $\tilde{v}_{kl}^{\rho\sigma}$ can be considered as the full effective interaction, which for simplicity is supposed to be pairwise, just as the “true” interaction $v_{kl}^{\rho\sigma}$ in the hamiltonian (4). The operator $\hat{E}_{pi, v j}^{in}$ in (18) (describing that part of the initial configurational energy which depends on occupations of sites i and j) can be expressed in terms of formal variational derivatives of the hamiltonian (3) over n_{pi} and n_{vj} , $H_{pi}^t = \delta H^t / \delta n_{pi}$ and $H_{pi, v j}^t = \delta^2 H^t / \delta n_{pi} \delta n_{vj}$:

$$\hat{E}_{pi, v j}^{in} = n_{pi} H_{pi}^t + n_{vj} H_{vj}^t - n_{pi} n_{vj} H_{pi, v j}^t \quad (20)$$

where the third term corresponds to the subtraction of the “double-counted” interaction between an atom p at site i and a vacancy v at site j .

The main idea of further manipulations (analogous to those made in [10, 11]) is to reduce the averages of complex operators in square brackets in (18) to some more simple averages having a clear physical meaning. To this end, in sums over all configurations $\{n_k^\rho\}$ in (18) we first perform summation over all possible occupations of only two sites, i and j , belonging to the ij bond under consideration. Due to the presence in (18) of the projection operator $n_i^p n_j^v$, the summation reduces to putting $n_i^q = \delta_{qp}$ and $n_j^\rho = \delta_{\rho v}$ in the n_i^q - and n_j^ρ -dependent exponential factor $\exp Y$ multiplied by this projection operator, where

$$Y = \beta(E_{pi, v j}^{in} - H_{eff}). \quad (21)$$

Note that the saddle-point energy $\hat{E}_{pi, v j}^{SP}$, according to its definition (10), does not contain operators of occupations of site i and j . Therefore, the common factor $\omega_{pv}^{eff} \exp(\beta\Omega - \beta \hat{E}_{pi, v j}^{SP})$ will be skipped for brevity in Eqs. (23)-(26).

For what follows it is convenient to restore formally the summation over all occupation number sets $\{n_k^\rho\}$ in (18), including all values of n_i^ρ and n_j^σ . To this end we can introduce the operator $n_i^h n_j^h$ in the summand. Since this projection operator is nonzero only when all n_i^ρ and n_j^σ are zero, the summation with this factor over all possible occupations of

sites i and j is equivalent to omitting all n_i^ρ - and n_j^σ -dependent terms in the exponential $\exp Y$. Therefore, the result of the summation can be written as

$$\sum_{n_i^\rho, n_j^\sigma} n_i^p n_j^v \exp Y = \sum_{n_i^\rho, n_j^\sigma} n_i^h n_j^h \exp (Y_{pi} + Y_{vj} + Y_{pi,vj} + Y) \quad (22)$$

Here Y_{pi} , Y_{vj} and $Y_{pi,vj}$ are the variational derivatives of the operator Y over the relevant occupation numbers: $Y_{pi} = \delta Y / \delta n_i^p$, etc. The first term of the exponential in Eq. (22) corresponds to the contribution to the sum (22) of the term in Y linear in n_i^p but not in n_j^v , the second, to that of the term in Y linear in n_j^v but not in n_i^p , and the third, to that of the term in Y linear in both n_i^p and n_j^v .

Let us first consider in (22) the term with $p = \alpha$ and express all operators n_l^h in the expression (20) for $E_{\alpha i, v j}^{in}$ via the independent n_l^ρ using Eq. (1). After the above-mentioned putting in this expression $n_i^\alpha = 1$, $n_j^v = 1$, the exponent Y in (21) takes the form

$$Y = \beta \left[\sum_{l\rho} \left(V_{il}^{\alpha\rho} - V_{il}^{\alpha h} \right) n_l^\rho + \sum_{l\rho} \left(V_{jl}^{v\rho} - V_{jl}^{v h} \right) n_l^\rho + \sum_l \left(V_{il}^{\alpha h} + V_{jl}^{v h} \right) - V_{ij}^{\alpha v} - H_{eff} \right]. \quad (23)$$

Using Eqs. (19) and (5) we can explicitly write the relation (22) at $p = \alpha$ as follows:

$$\begin{aligned} \sum_{n_i^\rho, n_j^\sigma} n_i^\alpha n_j^v \exp Y = \sum_{n_i^\rho, n_j^\sigma} n_i^h n_j^h \exp \left\{ \beta \left[\sum_{l\rho} (u_{il}^\rho + u_{jl}^\rho) n_l^\rho + \sum_l \left(V_{il}^{\alpha h} + V_{jl}^{v h} \right) - V_{ij}^{h h} - h_{ij}^{\alpha v} \right. \right. \\ \left. \left. + \lambda_i^\alpha + \left(\lambda_j^v - \sum_{l\rho} h_{jl}^{v\rho} n_l^\rho \right) - H_{eff} \right] \right\} \end{aligned} \quad (24)$$

where the quantity

$$u_{il}^\rho = (V_{il}^{\rho h} - V_{il}^{h h}) \quad (25)$$

can be called “the kinetic interaction” for a ρ -species atom (as it influences only mobilities but not thermodynamic properties [15]). Note that the vacancy concentration $c_i^v = \langle n_i^v \rangle$ in real substitution alloys is very small, hence all n_l^v can be neglected in the statistical averages which enter Eqs. (18). Therefore, terms with n_l^ρ in (24) correspond actually to the minority atoms with $\rho = \beta \neq v$. In writing Eq. (24) we also used the above-mentioned considerations that for the usual conditions of phase transformations, the significant renormalizations $h_{ij}^{v\alpha}$ can be expected only for the vacancy-atom interactions, while for the interactions between different atoms, the analogous renormalizations $h_{ij}^{\alpha\beta}$ are not essential.

In the case $p = h$, Eq. (22) is simplified as the operator Y in (21) depends only on the independent operators n_j^ρ but not on n_i^h . Therefore, terms Y_{hi} and $Y_{hi,vj}$ in (22) are absent, and the exponent is reduced to $(Y_{vj} + Y)$. Making the same manipulations as described above, we obtain for this case instead of (24):

$$\begin{aligned} \sum_{n_i^\rho, n_j^\sigma} n_i^h n_j^v \exp Y = \sum_{n_i^\rho, n_j^\sigma} n_i^h n_j^h \exp \left\{ \beta \left[\sum_{l\beta} (u_{il}^\beta + u_{jl}^\beta) n_l^\beta + \sum_l \left(V_{il}^{h h} + V_{jl}^{v h} \right) - V_{ij}^{h h} \right. \right. \\ \left. \left. + \left(\lambda_j^v - \sum_{l\beta} h_{jl}^{v\beta} n_l^\beta \right) - H_{eff} \right] \right\}. \end{aligned} \quad (26)$$

Substituting relations (24) and (26) in (18) we can express the derivatives dc_i^ρ/dt via some statistical averages. In writing these averages we can take into account that the interaction renormalizations \hat{h}_{int} in (12) are present only for the vacancy-atom terms

$h_{ij}^{v\beta} n_i^v n_j^\beta$ which include the vacancy occupation operators n_i^v and thus can be neglected. Therefore, the quasi-equilibrium distribution (15) can be used in calculations of these averages. To simplify formulas, in treatment of interaction renormalization terms $h_{jl}^{v\beta} n_l^\beta$ in Eqs. (24) and (26) we will use the mean-field approximation (MFA), replacing each operator n_l^β in these averages by its mean value c_l^β . Therefore, each term $h_{jl}^{v\beta} n_l^\beta$ is replaced by $h_{jl}^{v\beta} c_l^\beta$, which corresponds to replacing the vacancy site chemical potential λ_i^v by its “renormalized” value $\tilde{\lambda}_i^v$:

$$\left(\lambda_i^v - \sum_{l\beta} h_{jl}^{v\beta} n_l^\beta \right) \rightarrow \tilde{\lambda}_i^v = \left(\lambda_i^v - \sum_{l\beta} h_{jl}^{v\beta} c_l^\beta \right). \quad (27)$$

In Sec. 2.2 we show that at c_l^β values close to unity, when the interaction renormalization effects can be expected to be most significant, the approximation (27) becomes exact. Hence, one can expect it to be sufficiently accurate at all c_l^β . We can also note that a similar MFA treatment of interaction renormalization effects have been used by Nastar et al. [11, 13], and comparing their MFA and kinetic Monte Carlo results, these authors found the MFA accuracy to be sufficient for treatments of the renormalization effects.

Using relations (24)-(27) we can write Eqs. (18) in the concise form

$$\begin{aligned} dc_i^\alpha/dt &= \sum_{j(i)} \gamma_{\alpha v} b_{ij}^\alpha (\xi_i^v \eta_j^\alpha - \xi_j^v \eta_i^\alpha) \\ dc_i^v/dt &= \sum_{j(i)} \left[\xi_j^v \left(\gamma_{hv} b_{ij}^h + \sum_{\beta} \gamma_{\beta v} b_{ij}^\beta \eta_i^\beta \right) - \{i \rightarrow j\} \right] \end{aligned} \quad (28)$$

which will be called the “quasi-equilibrium” kinetic equations (QKE). The term γ_{pv} in these equations (where p is α or h , i. e. denotes a minority or host atom) is the effective exchange rate $p \rightleftharpoons v$ for a pure host metal. This term can be written in the form similar to Eq. (7):

$$\gamma_{pv} = \omega_{pv}^{eff} \exp(-\beta E_{ac}^{pv}) \quad (29)$$

where ω_{pv}^{eff} is the same as in (8), while E_{ac}^{pv} is the effective activation energy which is expressed via the saddle point energies E_h^p in (11) and interactions $V_{ij}^{p'q'}$ and $h_{ij}^{\alpha v}$ in (3) and (19) as follows:

$$E_{ac}^{\alpha v} = E_h^p - \sum_j (V_{ij}^{ph} + V_{ij}^{vh}) + V_{nn}^{hh} + h_{ij}^{\alpha v} \quad (30)$$

$$E_{ac}^{hv} = E_h^h - \sum_j (V_{ij}^{hh} + V_{ij}^{vh}) + V_{nn}^{hh} \quad (31)$$

where nn means “nearest neighbors”. Comparing these expressions to the analogous activation energies $E_{ac,MC}^{pv}$ used in the kinetic Monte Carlo approach [14] and given by Eq. (2.5) in [26], we find:

$$E_{ac}^{\alpha v} = E_{ac,MC}^{\alpha v} + \tilde{v}_{nn}^{\alpha v}; \quad E_{ac}^{hv} = E_{ac,MC}^{hv} \quad (32)$$

where $\tilde{v}^{\alpha v}$ is the same as in (19). The difference between $E_{ac}^{\alpha v}$ and $E_{ac,MC}^{\alpha v}$ arises because in the statistically averaged QKE (28), the transition probability (7) is averaged over the distribution (12). For the inter-site exchange $\alpha i \rightleftharpoons v j$, it leads to an extra Gibbs factor $\exp(-\beta \tilde{v}_{ij}^{\alpha v})$ with $\tilde{v}_{ij}^{\alpha v}$ from (19) in the averaged probability.

In this connection we note that in their study of diffusion in dilute Fe-Cu alloys [14] with a thorough taking into account the correlation effects for this vacancy-mediated diffusion [27], SF obtained for an effective activation energy of a copper atom the value $(E_{ac}^{Cu})_{eff} \simeq 0.47$ eV [26, 28]. This is very close to the value $E_{ac}^{Cu} = 0.44$ eV which follows from Eq. (30) at $h_{ij}^{Cu} = 0$ after substitution of couplings V_{ij}^{pq} used by SF. It may imply that for the diffusion in dilute Fe-Cu alloys, our statistical averaging with the quasi-equilibrium Gibbs distribution (15) can rather accurately describe the correlation effects mentioned [27], while the interaction renormalization effects for this diffusion are not very significant.

The quantities b_{ij}^p in (28) (to be called “correlators”) are certain averages of site occupations which describe influence of minority atoms in vicinity of the bond ij on the $pi \rightleftharpoons vj$ jump probability:

$$b_{ij}^p = \langle n_i^h n_j^h \exp \left[\sum_{\alpha l} \beta (u_{il}^\alpha + u_{jl}^\alpha) n_l^\alpha - \sum_{\alpha, l=l_{nn}^{ij}} \beta \Delta_\alpha^p n_l^\alpha \right] \rangle \quad (33)$$

where Δ_α^p is the same as in (11), and u_{il}^α is the same as in (24)-(26).

Finally, the quantities ξ_i^v and η_i^α in (28) can be called the “site thermodynamic activities” for vacancies and α -species atoms, respectively, because they are related to the site chemical potentials λ_i^α in (15) and the renormalized site chemical potential $\tilde{\lambda}_i^v$ in (27) as

$$\xi_i^v = \exp(\beta \tilde{\lambda}_i^v); \quad \eta_i^\alpha = \exp(\beta \lambda_i^\alpha), \quad (34)$$

that is, similarly to the relations between conventional thermodynamic activities and chemical potentials.

2.2 Calculations of site chemical potentials λ_i^ρ and correlators b_{ij}^p

To find explicit expressions for site chemical potentials $\lambda_i^\rho = \lambda_i^\rho(c_j)$ determined by Eqs. (17), and for correlators $b_{ij}^p = b_{ij}^p(c_k)$ determined by Eqs. (33), we should use some approximate method of statistical physics, such as the MFA or cluster methods [12]. As discussed in detail in [15, 21, 29], employing the MFA for calculations of chemical potentials λ_i^ρ in real alloys often leads to great errors, while the pair cluster approximation (PCA) usually combines simplicity of calculations with a high accuracy, particularly for dilute alloys. As an illustration (used also below for interstitial alloys), we present the PCA expressions for λ_i^ρ in a binary A-B- v alloy with host atoms $h=A$ and minority atoms $\alpha=B$ (skipping index B at $\lambda_i^B = \lambda_i$ and $c_i^B = c_i$ for brevity):

$$\lambda_i = T \left[\ln(c_i/c_i^h) + \sum_{j \neq i} \ln(1 - g_{ij} c_j) \right] \quad (35)$$

$$\lambda_i^v = T \left[\ln(c_i^v/c_i^h) - \sum_{j \neq i} \ln(1 + g_{ij}^v c_j^\alpha) \right]. \quad (36)$$

Here the function g_{ij} or g_{ij}^v is expressed via the Mayer function $f_{ij} = [\exp(-\beta v_{ij}) - 1]$ or $f_{ij}^v = [\exp(-\beta v_{ij}^{vB}) - 1]$ for the potential $v_{ij} \equiv v_{ij}^{BB}$ or v_{ij}^{vB} defined in (5) as follows:

$$\begin{aligned} g_{ij} &= 2f_{ij}/[R_{ij} + 1 + f_{ij}(c_i + c_j)] \\ g_{ij}^v &= 2f_{ij}^v/[R_{ij} + 1 + f_{ij}(c_i - c_j)] \\ R_{ij} &= \{[1 + (c_i + c_j)f_{ij}]^2 - 4c_i c_j f_{ij}(f_{ij} + 1)\}^{1/2}. \end{aligned} \quad (37)$$

For a multicomponent alloy A-B₁...B_m-v, the PCA methods of calculations of site chemical potentials λ_i^p are described in [21].

In calculations of correlators b_{ij}^p (33), we first consider for simplicity the case of configuration-independent saddle-point energies when differences $\hat{\Delta}_\alpha^p$ and Δ_α^p in Eqs. (10), (11) and (33) are zero and correlators $b_{ij}^p = b_{ij}$ are independent of the kind of a jumping atom p . Using Eqs. (2) and the identity

$$\exp(xn_l^\alpha) = 1 + n_l^\alpha f(x), \quad f(x) = (e^x - 1), \quad (38)$$

which follows from (2), we can rewrite Eq. (33) as

$$\begin{aligned} b_{ij} &= \left\langle n_i^h n_j^h \prod_{l=1}^{k_t} (1 + \sum_{\alpha} f_l^\alpha n_l^\alpha) \right\rangle = \\ &= \sum_{k=0}^{k_t} \sum_{l_1 \neq \dots l_k} \sum_{\alpha_1 \dots \alpha_k} \left\langle n_i^h n_j^h n_{l_1}^{\alpha_1} \dots n_{l_k}^{\alpha_k} \right\rangle f_{l_1}^{\alpha_1} \dots f_{l_k}^{\alpha_k} \end{aligned} \quad (39)$$

where we set

$$f_l^\alpha = f(\beta u_{il}^\alpha + \beta u_{jl}^\alpha) \quad (40)$$

with $f(x)$ from (38), while k_t in (39) is the total number of sites with nonzero values of potentials $(u_{il}^\alpha + u_{jl}^\alpha)$. For example, for the nearest-neighbor or next-to-nearest-neighbor interaction models in a BCC lattice [15], we have $k_t = 14$ or $k_t = 20$.

In finding averages in (39) we should consider that the functions f_l^α in Eqs. (39) and (40) for real alloys are typically rather large. For example, for the BCC Fe-Cu- v alloys considered in [15] we have: $f(\beta u_1) \sim 5$ and $f(\beta u_2) \sim 1$ (where interaction u_1 and u_2 corresponds to the nearest and next-to nearest neighbors). Thus the main contributions to sum (39) come from averages of products of many different operators n_l^α corresponding to well-separated and weakly correlated sites l . In particular, for the BCC lattice, these products (even for the nearest-neighbor interaction model) include terms with the neighbors from first to tenth, most often third and fourth. Correlations of occupations of so distant sites should typically be weak. Therefore, using the simple MFA that neglects such correlations, in calculations of averages (39) should, generally, be adequate, unlike calculations of chemical potentials λ_i mentioned above.

In the MFA, each operator n_l^p in Eq. (39) is replaced by its average value c_l^p . Hence the correlator b_{ij} can be explicitly written as

$$b_{ij} = c_i^h c_j^h \prod_{l=1}^{k_t} (1 + \sum_{\alpha} c_l^\alpha f_l^\alpha) = c_i^h c_j^h \exp \left[\sum_{l=1}^{k_t} \ln \left(1 + \sum_{\alpha} f_l^\alpha c_l^\alpha \right) \right]. \quad (41)$$

When the differences Δ_α^p in Eqs. (11) and (33) are nonzero, the correlator b_{ij}^p in Eq. (33) can be calculated by the same way as b_{ij} in (39)-(41). The difference arises only for sites $l = l_{nn}^{ij}$ adjacent to the ij bond, for which the factor f_l^α defined by Eq. (40) is replaced by an analogous factor $f_{l\Delta}^{\alpha p}$ defined as

$$f_{l\Delta}^{\alpha p} = f(\beta u_{il}^\alpha + \beta u_{jl}^\alpha - \beta \Delta_{\alpha l}^p \delta_{l, l_{nn}^{ij}}) \quad (42)$$

where $\Delta_{\alpha l}^p = \Delta_\alpha^p \delta_{l, l_{nn}^{ij}}$ and $\delta_{l, l_{nn}^{ij}}$ is unity when $l = l_{nn}^{ij}$ and zero when $l \neq l_{nn}^{ij}$. Therefore, the correlator b_{ij}^p is given by Eq. (41) with replacing each f_l^α by $f_{l\Delta}^{\alpha p}$:

$$b_{ij}^p = c_i^h c_j^h \exp \left[\sum_{l=1}^{k_t} \ln \left(1 + \sum_{\alpha} f_{l\Delta}^{\alpha p} c_l^\alpha \right) \right]. \quad (43)$$

Finally, let us make a remark about the MFA-type approximation (27) used above in the derivation of QKE (28). If we don't use this approximation, Eqs. (28), instead of the correlators b_{ij}^p (43), include similar correlators \tilde{b}_{ij}^p differing from b_{ij}^p by the presence of additional interaction renormalization terms $\beta h_{jl}^{v\beta} n_l^\alpha$ in the exponents:

$$\tilde{b}_{ij}^p = c_i^h c_j^h \exp \sum_{l=1}^{k_t} \ln \left\{ 1 + \sum_{\alpha} \left[\exp \left(\beta u_{il}^\alpha + \beta u_{jl}^\alpha - \beta \Delta_{\alpha l}^p - \beta h_{jl}^{v\alpha} \right) - 1 \right] c_l^\alpha \right\} \quad (44)$$

where we write the function $f(x)$ from (38) explicitly. For the diffusional transformations under consideration, the interaction renormalization effects seem to be most significant in those space regions where the local concentration c_l^α is close to unity. It is illustrated by the case of precipitation in Fe-Cu alloys where these effects arise due to the strong trapping of vacancies by the Cu-based precipitates for which c_l^{Cu} is close to unity [15]. For such c_l^α , the argument of logarithm in (44) is reduced to the single exponent, and the relation (27) becomes exact. Let us also note that for the simulations of diffusional transformations based on Eq. (28), the details of vacancy distributions are actually insignificant due to the ‘‘adiabaticity principle’’ and the ‘‘rescaling of time’’ procedure discussed in Sec. 2.3. Therefore, the approximation (27) appears to be sufficient for using in such simulations.

2.3 Reducing kinetic equations (28) to those for some direct exchange model

The QKE (28) can be used for modeling of most different phase transformations, in particular, of processes of precipitation which attract great attention in connection with numerous applications [30, 31, 32]. However, in the original form (28) these equations are not suitable for using in computer simulations due to very small values of vacancy concentration c_v in real alloys. As atomic exchanges $pi \rightleftharpoons vj$ take place only with a vacancy, this smallness leads to a great difference in the relaxation time τ between atoms α and vacancies v : $\tau_\alpha \sim \tau_v / c_v \gg \tau_v$. It is illustrated by the presence of vacancy activities $\xi_i^v = \exp(\beta \tilde{\lambda}_i^v)$ in the right-hand side of the QKE (28). This activity is proportional to the vacancy concentration c_i^v which is a general relation of thermodynamics of dilute solutions illustrated by Eq. (36). Therefore, the time derivatives of mean occupations are proportional to the local vacancy concentration, c_i^v or c_j^v . It is natural for the vacancy-mediated kinetics and leads to the strong inequality between τ_α and τ_v mentioned above. Therefore, the type of temporal evolution for atoms and vacancies is quite different, which makes the direct numerical solving of Eqs. (28) for $c_i^v(t)$ and $c_i^\alpha(t)$ to be unsuitable and time consuming.

At the same time, the inequality $\tau_\alpha \gg \tau_v$ enables us to use the ‘‘adiabatic’’ approach used in many fields of physics, including the well-known Born-Oppenheimer approach in the quantum-mechanical description of motion of atoms in molecules and solids. In this approach, the effective driving force for a slow motion is obtained by its averaging over a rapid motion. Therefore, to fully describe the slow motion, only few averaged characteristics of the rapid motion are needed. In the quantum mechanics, this is the appropriate electronic energy (‘‘electronic term’’) calculated at the fixed positions \mathbf{R}_i of atoms. In our problem it means that at the given atomic distribution $\{c_i^\alpha\}$, the local vacancy concentration c_i^v adiabatically fast (i. e., for a time $\tau_v \sim c_v \tau_\alpha \ll \tau_\alpha$) reaches its ‘‘quasi-equilibrium’’ value $c_i^v \{c_i^\alpha\}$ for which the right-hand side of the second equation (28) vanishes. Therefore, discarding small corrections of the relative order $c_i^v \ll 1$, we

can approximate this equation by its adiabatic version:

$$0 = \sum_{j(i)} \left[\xi_j^v \left(\gamma_{hv} b_{ij}^h + \sum_{\alpha} \gamma_{\alpha v} b_{ij}^{\alpha} \eta_i^{\alpha} \right) - \{i \rightarrow j\} \right] \quad (45)$$

which can be called “the adiabaticity equation” for the vacancy activity ξ_i^v . Solving this linear equation for ξ_i^v we can, in principle, express it via c_j^{α} . Then substitution of these $\xi_i^v(c_j^{\alpha})$ into the first Eq. (28) yields the QKE for some equivalent direct-atomic-exchange (DAE) model.

To illustrate these considerations, we first consider the models with the configuration-independent saddle-point energies. For such models, the parameters Δ_p^p in (11) are zero, the correlators $b_{ij}^p = b_{ij}$ do not depend on the kind p of a jumping atom, and the adiabaticity equation (45) takes the simple form:

$$\sum_{j(i)} b_{ij} \xi_i^v \xi_j^v \left[\left(\gamma_{hv} + \sum_{\alpha} \gamma_{\alpha v} \eta_i^{\alpha} \right) / \xi_i^v - \{i \rightarrow j\} \right] = 0 \quad (46)$$

If we let $1/\nu_i$ denote the first term in the square brackets (46), then the difference in these brackets takes the form $(\nu_i^{-1} - \nu_j^{-1})$. Hence, a solution of Eqs. (46) is given by ν_i being a constant independent of the site number i (although possibly depending on time as well as on temperature and other external parameters):

$$\nu_i = \xi_i^v / \left(\gamma_{hv} + \sum_{\alpha} \gamma_{\alpha v} \eta_i^{\alpha} \right) = \nu(t). \quad (47)$$

Relation (47) determines the above “quasi-equilibrium” vacancy distribution $c_i^v \{c_i^{\alpha}\}$ which adiabatically fast follows the atomic distribution $\{c_i^{\alpha}\}$. Substituting it in the first Eq. (28) we obtain an explicit kinetic equation for atomic distributions $\{c_i^{\alpha}\}$ for which the evolution of the vacancy distribution is characterized by a single parameter $\nu(t)$ being a “spatially self-averaged” quantity:

$$\begin{aligned} dc_i^{\alpha}/dt = & \sum_{j(i)} b_{ij} \nu(t) \left[\gamma_{\alpha v} \gamma_{hv} (\eta_j^{\alpha} - \eta_i^{\alpha}) \right. \\ & \left. + \sum_{\beta} \gamma_{\alpha v} \gamma_{\beta v} (\eta_j^{\alpha} \eta_i^{\beta} - \eta_i^{\alpha} \eta_j^{\beta}) \right]. \end{aligned} \quad (48)$$

Equations (48) can also be rewritten in the form used for DAE models [12]:

$$\begin{aligned} dc_i^{\alpha}/dt = & \sum_{j(i)} M_{ij}^{\alpha h} 2 \sinh[\beta(\lambda_j^{\alpha} - \lambda_i^{\alpha})/2] \\ & + \sum_{j(i), \beta} M_{ij}^{\alpha \beta} 2 \sinh[\beta(\lambda_j^{\alpha} + \lambda_i^{\beta} - \lambda_i^{\alpha} - \lambda_j^{\beta})/2] \end{aligned} \quad (49)$$

where the generalized mobilities M_{ij}^{pq} , which describe the inter-site exchanges $\alpha \rightleftharpoons h$ and $\alpha \rightleftharpoons \beta$, are given by

$$M_{ij}^{\alpha h} = \gamma_{\alpha v} \gamma_{hv} \nu(t) b_{ij} \exp [\beta(\lambda_i^{\alpha} + \lambda_j^{\alpha})/2] \quad (50)$$

$$M_{ij}^{\alpha \beta} = \gamma_{\alpha v} \gamma_{\beta v} \nu(t) b_{ij} \exp [\beta(\lambda_i^{\alpha} + \lambda_j^{\alpha} + \lambda_i^{\beta} + \lambda_j^{\beta})/2]. \quad (51)$$

Comparing these expressions with the expression (32) in [10] which describes the mobility M_{ij}^{pq} in an alloy with the nearest-neighbor direct-exchange rate $\gamma_{ij}^{pq} = \gamma_{pq}$, we see that Eqs. (50) and (51) correspond to a DAE model with the effective direct exchange rates

$$\gamma_{\alpha h}^{eff} = \gamma_{\alpha v} \gamma_{hv} \nu(t); \quad \gamma_{\alpha \beta}^{eff} = \gamma_{\alpha v} \gamma_{\beta v} \nu(t). \quad (52)$$

As $\nu(t)$ in (47) is proportional to c_i^v , the effective DAE rates (52) are by a factor c_v smaller than the vacancy exchange rates γ_{pv} , in accordance with the above-discussed adiabaticity relations.

For more realistic models with configuration-dependent saddle-point energies, the basic adiabaticity equation (45) for vacancy activities ξ_i^v can not be solved analytically in general, and hence either numerical or some approximate analytic methods should be used. For the first-principle model of Fe-Cu- v alloys developed in [14], such approximate treatments made in [15] have shown that the equivalence relations (48)-(52) usually preserve their form, but the correlator b_{ij} is replaced by some other quantity, b_{ij}^{Cu} or b_{ij}^{Fe} . Physically, the possibility to reduce the vacancy-mediated kinetics to the equivalent direct atomic exchange kinetics is connected with the above-mentioned fact that in the course of evolution of an alloy, the distribution of vacancies adiabatically fast follows that of the main components. Therefore, it can be assumed that this equivalence is actually a general feature of the vacancy-mediated kinetics, while for more general models, the correlators b_{ij} in (50) can be replaced by some other expressions with similar properties.

The function $\nu(t)$ in Eq. (52) determines the rescaling of time between the initial vacancy-mediated exchange model and the equivalent DAE model (48)-(52). Temporal evolution of this DAE model is actually described by the dimensionless “reduced time” t_r related to the real time t by the differential or integral relations

$$\begin{aligned} dt_r &= \gamma_{\alpha h}^{\text{eff}} dt = \gamma_{\alpha v} \gamma_{h v} \nu(t) dt, & t_r &= \int_0^t \gamma_{\alpha h}^{\text{eff}}(t') dt', \\ t &= \int_0^{t_r} dt'_r \tau_{\alpha h}^{\text{eff}}(t'_r) \end{aligned} \quad (53)$$

where $\tau_{\alpha h}^{\text{eff}} = 1/\gamma_{\alpha h}^{\text{eff}}$ has the meaning of the mean time of an atomic exchange $\alpha \rightleftharpoons h$, while t_r has the meaning of an effective number of such atomic exchanges.

The form of the function $t(t_r)$ in (53) depends on the boundary conditions for vacancies adopted in simulations. In particular, if we adopt the “vacancy conservation” model for which the interaction renormalization effects can be expected to be insignificant, we can use Eqs. (47) and (36) to express the local vacancy concentration c_i^v via $\nu(t)$ and $c_i^\alpha(t_r)$. Then the vacancy conservation condition: $\sum_i c_i^v(t, t_r) = N_v = \text{const}$, can be used to explicitly find the dependence $t(t_r)$. However, taking into account a possible creation of vacancies at various lattice defects (grain boundaries, dislocations, etc) suggested in the kinetic Monte Carlo (KMC) simulations [14, 26] appears to be more realistic. Then the dependences $t(t_r)$ can be found from comparison of results of the DAE-based simulations described above to the appropriate KMC results, as illustrated in [15], and these dependences seem to be rather simple and universal. In more detail, applications of Eqs. (48)-(53) to studies of precipitation in concrete alloys will be described elsewhere.

3 EQUATIONS FOR DIFFUSION OF INTERSTITIAL ATOMS IN INTERSTITIAL ALLOYS

In binary interstitial alloys Me-X where X is an interstitial atom, in particular, in iron-carbon steels, diffusion of atoms X is realized via thermo-activated jumps of these atoms between their interstitial sites (“pores”). Therefore, this diffusion can be described by the general equations of Sec. 2 for a particular case of a substitution binary alloy X- v which consists of atoms $\alpha=X$ and vacancies v in the crystal lattice of pores, with the “host”

atoms h being vacancies v . The total configurational Hamiltonian (3) here includes X-X interactions between atoms X, but not X- v and v - v interactions. Therefore, only V_{ij}^{XX} terms are nonzero in formulas (3)-(5):

$$V_{ij}^{\alpha\alpha} = V_{ij}^{XX} \neq 0, \quad V_{ij}^{\alpha h} = V_{ij}^{hh} = 0. \quad (54)$$

The only meaningful index $\alpha=X$ is usually skipped below, for example: $c_i^X = c_i$, $V_{ij}^{XX} = v_{ij}$, thus the effective Hamiltonian (19) takes the form:

$$H_{eff} = - \sum_i \lambda_i n_i + H_{int}, \quad H_{int} = \frac{1}{2} \sum_{ij} v_{ij} n_i n_j. \quad (55)$$

The mean occupation $c_i = \langle n_i \rangle$ of pore i by an atom X is related to the local chemical concentration x_i by the relation depending on the geometry of pores [2], e. g. $c=x/(1-x)$ for a uniform austenite structure MeX_c with the FCC lattice of octo-pores.

An important principal feature differing the diffusional kinetics in the interstitial Me-X (i. e., substitution X- v) alloys from that in the substitution A-B- v alloys is the validity for Me-X alloys of relation (14), that is, the absence of interaction renormalization effects. It follows, first, from the physical considerations presented after Eqs. (14) and (15) and, second, from the thorough analysis of interaction renormalization effects for A-B- v alloys made by Nastar et al [11, 13]. These authors found these effects to be described by the terms antisymmetric with respect to interchanging A and B atoms, $(h_{ij}^{AB} - h_{ij}^{BA})$, which vanish in a binary X- v alloy where A=B=X. Therefore, the diffusional kinetics in Me-X alloys can be described by the quasi-equilibrium relations (14) and (15).

For a uniform Me-X alloy, the site chemical potential $\lambda_i=\lambda$ in (55) coincides with the thermodynamic chemical potential μ_X , unlike substitution alloys where the analogous quantity λ_α , as mentioned in Sec. 2.1, is equal to the difference $(\mu_\alpha - \mu_h)$. To show it, we generalize Eqs. (21)-(24) and (40)-(43) of Ref. [21] to the case of interstitial alloys Me-X. The quasi-equilibrium Gibbs distribution (15) and the generalized grand canonical potential Ω_g for the effective Hamiltonian (55) have the form

$$P = \exp \left[\beta (\Omega_g + \sum_{\alpha i} \lambda_{\alpha i} n_{\alpha i} - H_{int}) \right], \quad (56)$$

$$\Omega_g = -T \ln \sum_{\{n_{\alpha i}\}} \exp \left[\beta \left(\sum_{\alpha i} \lambda_{\alpha i} n_{\alpha i} - H_{int} \right) \right], \quad (57)$$

while the mean occupation c_i is related to $\Omega_g\{\lambda_{\alpha i}\}$ by the formula obtained by the differentiation of equality (57):

$$c_i = \langle n_i \rangle = -\partial \Omega_g / \partial \lambda_i. \quad (58)$$

Therefore, if we define the generalized free energy F by the equality

$$F = \Omega_g + \sum_i \lambda_i c_i, \quad (59)$$

then site chemical potential λ_i is related to F by the relations generalizing a similar relation for a uniform alloy:

$$\lambda_i = \partial F / \partial c_i. \quad (60)$$

To relate λ_i and Ω_g in Eqs. (56)-(60) to the thermodynamic chemical potentials, we consider the case of a uniform alloy Me-X when c_i and λ_i in Eqs. (56)-(60) are independent

of i : $c_i = c$, $\lambda_i = \lambda$. For definiteness, we discuss the austenite structure for which the total number of interstitial sites (octo-pores) is equal to the total number N_{Me} of Me atoms. Then instead of the total thermodynamic potentials, Ω_g and F , it is convenient to consider the analogous quantities per one atom Me, Ω and f :

$$\Omega = \Omega_g/N_{\text{Me}}, \quad f = F/N_{\text{Me}} = \Omega + \lambda c, \quad c = N_{\text{X}}/N_{\text{Me}}. \quad (61)$$

Here N_{X} is the total number of atoms X, thus c is the mean occupation of an interstitial site, and, according to Eq. (60):

$$\lambda = \partial f / \partial c. \quad (62)$$

The quantities Ω and λ in Eqs. (61) and (62) are simply related to the partial chemical potentials, μ_{X} and μ_{Me} , defined by the thermodynamic relations:

$$\mu_{\text{X}} = \partial F / \partial N_{\text{X}}, \quad \mu_{\text{Me}} = \partial F / \partial N_{\text{Me}}. \quad (63)$$

Substituting relations (61) for c and $F = N_{\text{Me}}f(c)$ in Eqs. (63) and taking into account Eq. (62), we obtain:

$$\lambda = \mu_{\text{X}}, \quad \Omega = \mu_{\text{Me}}. \quad (64)$$

Thus, the quantity λ or Ω in Eqs. (61) and (62) has the meaning of the chemical potential of atoms X or atoms Me, respectively.

Kinetic equation describing diffusion of atoms X in an interstitial alloy Me-X (treated as a binary substitution alloy X- v) can be obtained by substitution of relations (54) and (55) into the first Eq. (28):

$$dc_i/dt = \sum_{j(i)} \gamma_{ij} b_{ij}^{\text{X}} [\exp(\beta \lambda_j) - \exp(\beta \lambda_i)]. \quad (65)$$

Here we took into account that for a host atom $h = v$, the site chemical potential λ_i^h in (28) should be formally put zero, as illustrated by Eqs. (26) and (28). The jump probability γ_{ij} and the correlator b_{ij}^{X} in (65) are defined by the relations analogous to (29) and (33):

$$\gamma_{ij} = \omega_{ij}^{\text{eff}} \exp(-\beta E_{ac}^{ij}), \quad (66)$$

$$b_{ij}^{\text{X}} = \left\langle (1 - n_i)(1 - n_j) \exp \left(-\beta \sum_k \Delta_k^{ij} n_k \right) \right\rangle. \quad (67)$$

The pre-exponent ω_{ij}^{eff} in (66) is determined by Eq. (8) with replacing $p \rightarrow \text{X}$, while the activation energy E_{ac}^{ij} is reduced to the term $E_h^p = E_v^{\text{X}}$ in (10), unlike the more complex expression (31) in a substitutional alloy. Index “ ij ” at the quantities ω_{ij}^{eff} and E_{ac}^{ij} in (66) allows for a possible nonuniformity of an alloy; for a uniform alloy this index can be omitted. The quantity Δ_k^{ij} in (67) is the analogue of Δ_{ij}^p in Eqs. (10) and (11); it describes the change of the saddle point energy $E_{\text{Xi},vj}^{\text{SP}}$ for an inter-site X-atom jump $i \rightarrow j$ due to the presence of another atom X at site k .

The kinetic equation (65) can also be written in a form analogous to Eq. (49):

$$dc_i/dt = \sum_{j(i)} 2M_{ij} \sinh [\beta(\lambda_j - \lambda_i)/2] \quad (68)$$

where the generalized mobility M_{ij} , according to (65), is determined by the relation:

$$M_{ij} = \gamma_{ij} b_{ij}^{\text{X}} \exp [\beta(\lambda_i + \lambda_j)/2]. \quad (69)$$

In usual diffusion problems, the space dependence of functions $c_i = c(\mathbf{r}_i)$, $\lambda_i = \lambda(c_i)$, and $b_{ij}^X = b_{ij}^X(c_i, c_j)$ in Eqs. (65)-(69) is supposed to be smooth. Therefore, variations of these functions under replacing $c_i \rightarrow c_j$ (or $\mathbf{r}_i \rightarrow \mathbf{r}_j = \mathbf{r}_i + \mathbf{r}_{ji}$ where $\mathbf{r}_{ji} = \mathbf{r}_j - \mathbf{r}_i$ is the inter-pore distance) are small. Then the kinetic equation (65) or (68) can be expanded in powers of $\mathbf{r}_{ji} \nabla c$. It yields the continuous version of this kinetic equation having the form of the “continuity equation” for the flow \mathbf{j} of atoms X:

$$\partial c / \partial t + \text{div} \mathbf{j} = 0, \quad j_\alpha = - \sum_\nu D_{\alpha\nu}(c) \nabla_\nu c. \quad (70)$$

Here α and ν are Cartesian indices, and the diffusivity $D_{\alpha\nu}$ is determined by the following expression:

$$D_{\alpha\nu}(c) = \Gamma_{\alpha\nu} b_X \partial a_X / \partial c, \quad (71)$$

$$\Gamma_{\alpha\nu} = \frac{1}{2} \sum_{j(i)} \gamma_{ij} r_{ij}^\alpha r_{ij}^\nu \quad (72)$$

where $a_X = a_X(c, T) = \exp[\beta \lambda(c, T)]$ is the thermodynamic activity of X atoms, and $b_X = b_X(c, T)$ is the correlator b_{ij}^X in Eq. (67) at $c_i = c_j = c$.

The site chemical potential λ_i in a binary alloy can be written as

$$\lambda_i = \lambda_i^{id} + \lambda_i^{int} \quad (73)$$

where $\lambda_i^{id} = T \ln[c_i/(1 - c_i)]$ corresponds to the ideal solution, and λ_i^{int} describes inter-action effects, see, e. g., (35). Therefore, for the ideal solution for which both λ_i^{int} in (73) and Δ_l^{ij} in (67) are zero, we have: $a_X = c/(1 + c)$, $b_X = (1 - c)^2$, $b_X \partial a_X / \partial c = 1$, and Eq. (70) takes the form of a simple linear diffusion equation:

$$\partial c / \partial t = \sum_{\alpha\nu} D_{\alpha\nu}^{id} \nabla_{\alpha\nu}^2 c \quad (74)$$

with the concentration-independent diffusivity $D_{\alpha\nu}^{id}$ equal to $\Gamma_{\alpha\nu}$ in (72). However, when X-X interactions v_{ij} and Δ_l^{ij} are significant, the kinetic equation (70) is nonlinear, and the diffusivity \mathbf{D} in (71) should vary with the local concentration $c = c^X(\mathbf{r})$.

For a uniform cubic alloy, such as austenite, tensor $\Gamma_{\alpha\nu}$ is reduced to a scalar $\delta_{\alpha\nu} \gamma a^2$ where γ is given by Eq. (66) (with omission of index ij) and a is the FCC iron (γ -iron) lattice constant, hence $D_{\alpha\nu} = \delta_{\alpha\nu} D$. Then the diffusivity D , according to (71), can be written as

$$D = \gamma a^2 b_X \partial a_X / \partial c \quad (75)$$

where γ is defined by Eqs. (66) and (8) with the appropriate change of indices:

$$\gamma = \omega_X^{eff} \exp(-\beta E_{ac}), \quad \omega_X^{eff} = \omega_X \exp(\Delta S_X^{SP}). \quad (76)$$

For a uniform alloy with $c_i = c$, the PCA expression (35) for the local chemical potential $\lambda(c)$ is simplified [29]:

$$\begin{aligned} \lambda(c, T) &= T \sum_n z_n \ln(1 - g_n c), \quad g_n = 2f_n / (R_n + 1 + 2cf_n), \\ f_n &= \exp(-\beta v_n) - 1, \quad R_n = [1 + 4c(1 - c)f_n]^{1/2} \end{aligned} \quad (77)$$

where z_n is the coordination number, and v_n is the configurational interaction for the n th coordination sphere. In the case of weak interaction, $\beta v_n \ll 1$, Eq. (77) is reduced to the

MFA expression: $\lambda^{\text{MFA}} = (\sum_n z_n v_n) c$. However, for the realistic values of interactions v_n , such as those presented in Table 1 below, using the MFA can lead to significant errors [29].

Correlator $b_X(c, T)$ for a uniform alloy, according to Eqs. (67) and (44), can be written as

$$b_X(c, T) = (1 - c)^2 \exp \left[\sum_{n=1} z_n^{sp} \ln(1 + f_n^{sp} c) \right], \quad f_n^{sp} = \exp(-\beta \Delta_n) - 1 \quad (78)$$

where z_n^{sp} is the coordination number, and Δ_n is the saddle-point interaction for the n th coordination sphere of the saddle point considered. If these interactions are weak: $\beta \Delta_n \ll 1$, Eq. (78) takes its MFA form:

$$b_X(c, T) = (1 - c)^2 \exp \left(-\beta c \sum_{n=1} z_n^{sp} \Delta_n \right) \quad (79)$$

However, for the realistic saddle-point interactions Δ_n , such as those shown in Table 2 below, using the MFA can lead to significant errors, just as for λ in Eq. (77).

The microscopic relation (75) can be compared to various phenomenological models for diffusivity [1]-[4]. It can provide, in particular, the statistical expression for the phenomenological mobility M_{CVa} introduced by Ågren in his discussion of diffusion of carbon in austenite [1]-[3]. Comparing Eq. (75) to the definition of M_{CVa} by equation (9) in [2], we find:

$$M_{\text{CVa}} = \gamma a^2 b_X a_C / [c(1 - c) V_m T] \quad (80)$$

where V_m is the volume per atom Me. In more detail, the microscopic and phenomenological descriptions of diffusion of carbon in austenite are compared in Sec. 4.

Let us now consider a multicomponent interstitial alloy ($\text{Me}_1 \text{Me}_2 \dots$)-X with several species atoms p in the metal sublattice, such as an Fe-Mn-C alloy. The interstitial sites will be marked by indices i, j and k , while the sites in the metal sublattice, by indices l, m and n . The total configurational Hamiltonian can be written in the form generalizing Eq. (3):

$$H^t = \frac{1}{2} \sum_{ij} v_{ij} n_i n_j + \sum_{p, il} V_{il}^p n_i n_l^p + \frac{1}{2} \sum_{pq, lm} V_{lm}^{pq} n_l^p n_m^q \quad (81)$$

where we again skip index X for an interstitial atom putting $n_i^X = n_i$, $V_{il}^{Xp} = V_{il}^p$, $V_{ij}^{XX} = v_{ij}$. As above, we discuss diffusion of only interstitial but not metal atoms, and the presence of vacancies in the metal sublattice is neglected. Therefore, occupation operators n_l^h for host metal h can be expressed via those for the minority metals α similarly to Eq. (1): $n_l^h = (1 - \sum_{\alpha} n_l^{\alpha})$. The effective Hamiltonian for statistical averaging, instead of (19), takes the form:

$$\begin{aligned} H_{eff} = & - \sum_i \lambda_i n_i - \sum_{\alpha, l} \lambda_l^{\alpha} n_l^{\alpha} \\ & + \frac{1}{2} \sum_{ij} v_{ij} n_i n_j + \sum_{\alpha, il} v_{il}^{\alpha} n_i n_l^{\alpha} + \frac{1}{2} \sum_{\alpha\beta, lm} v_{lm}^{\alpha\beta} n_l^{\alpha} n_m^{\beta} \end{aligned} \quad (82)$$

where $v_{il}^{\alpha} = (V_{il}^{\alpha} - V_{il}^h)$, while $v_{lm}^{\alpha\beta}$ is related to V_{lm}^{pq} in (81) similarly to Eq. (5).

Equations describing diffusion of atoms X can be again derived using Eqs. (6)-(26) with appropriate generalizations and simplifications. In particular, the first equation (18) here takes the form

$$dc_i/dt = \sum_{\{n_k, n_l^{\alpha}\}} \sum_{j(i)} \omega_X^{eff} \left[(1 - n_i) n_j \exp(\beta \hat{E}_{ij}^{in} - \beta \hat{E}_{ij}^{SP}) - \{i \rightarrow j\} \right] \exp[\beta(\Omega - H_{eff})]. \quad (83)$$

Here the saddle-point energy \hat{E}_{ij}^{SP} , instead of Eqs. (10) and (11), is given by the expression

$$\hat{E}_{ij}^{SP} = E_h + \sum_k \Delta_k^{ij} n_k + \sum_{\alpha l} \Delta_{\alpha l}^{ij} n_l^\alpha \quad (84)$$

where Δ_k^{ij} and $\Delta_{\alpha l}^{ij}$ are analogues of Δ_k^{ij} in (67). Using relations (20) and (26), we again reduce Eq. (83) to the form (65). However, the activation energy E_{ac} in (66) and the correlator b_{ij}^X in (67) now are defined as

$$E_{ac} = E_h - \sum_l V_{il}^h, \\ b_{ij}^X = \left\langle (1 - n_i)(1 - n_j) \exp \left(-\beta \sum_k \Delta_k^{ij} n_k - \beta \sum_{\alpha l} \Delta_{\alpha l}^{ij} n_l^\alpha \right) \right\rangle, \quad (85)$$

and Eqs. (83) and (85) now include the statistical averaging over various distributions of α -species atoms in the metal sublattice.

4 CALCULATIONS OF DIFFUSIVITY AND ACTIVITY OF CARBON IN AUSTENITE FOR SIMPLE MODELS OF CARBON-CARBON INTERACTIONS

To calculate the diffusivity D according to the microscopic expression (75), we should use some theoretical model of X-X interactions in an alloy, for both the configurational interactions v_n in (77) which determine the chemical potential λ , and for the saddle-point interactions Δ_n in (78) which determine the correlator b_X . For substitution Fe-Cu alloys, such first-principle model for both v_n and Δ_n has been developed by SF [14], and simulations of precipitation in Fe-Cu alloys based on this model confirmed its adequacy and reliability [14]. For interactions of carbon in austenite, reliable first-principle calculations are still absent due to the well-known difficulties of taking into account magnetic interactions in γ -iron [19]. However, some simplified model of configurational interactions v_n in austenite has been suggested by Blanter [16], and his estimates of these interactions are presented in Table 1 as v_n^B . Below we use this model and some its extensions to investigate the concentration and temperature dependences of diffusivity D which follow from the microscopic expression (75).

Blanter used the model of purely deformational configurational interactions with the nearest-neighbor Kanzaki forces for all constants v_n^B except the first one. The nearest-neighbor constant v_1^B (which can not be adequately described by the deformational model due to the strong “chemical” repulsion at short C-C distances) was treated as a free parameter which was estimated from the fit of the carbon activity in austenite with respect to graphite, $a_C^{\gamma-gr}$, calculated with these v_n^B to the experimental values. The quantity $a_C^{\gamma-gr}$ is related to the “configurational” activity $a_C = \exp(\beta\lambda_C)$, where $\lambda_C = \lambda$ is the chemical potential of carbon in austenite discussed in Sec. 3, by the thermodynamic relation [16]:

$$a_C^{\gamma-gr} = a_C \exp(\beta\Delta G_C^{\gamma-gr}) \quad (86)$$

where $\Delta G_C^{\gamma-gr} = \Delta G_C^{\gamma-gr}(T)$ is the difference between the thermodynamic potentials per carbon atom in a pure γ -iron and in graphite. The fit to experimental $a_C^{\gamma-gr}(c, T)$ obtained

Figure 1: Dependence of carbon activity $a_C^{\gamma-gr}$ in austenite with respect to graphite on the carbon concentration $x_C = c/(1+c)$ for various temperatures T . Dots correspond to experimental data presented in [16]. Solid curves are calculated using the PCA expression (77) for λ with the interaction constants v_n from Table 1. Dashed curves are calculated using the phenomenological description of C-C interactions employed by Ågren [36].

Figure 2: Fe-C phase diagram. Dots correspond to experimental phase boundaries. Solid curves show ferrite-austenite phase boundaries calculated using Eq. (77) with v_n from Table 1. Dashed curves correspond to the phenomenological calculations by Ågren [36].

with the use for both Monte Carlo [16], and the PCA [29] calculations of $a_C(c, T)$ the v_n^B values, and for $\Delta G_C^{\gamma-gr}(T)$, some experimental estimates, seemed to be quite satisfactory. It may imply that the simple model of Blanter [16] can serve as a basis for realistic descriptions of C-C interactions in austenite.

Table 1. Configurational interactions v_n (in kelvin) of carbon atoms in austenite

n	1	2	3	4	5	6	7	8	9	10	11
$2\mathbf{R}_n/a$	110	200	211	220	310	222	321	400	330	411	420
R_n/R_1	1	1.41	1.73	2	2.24	2.45	2.65	2.83	3	3	3.16
z_n	12	6	24	12	24	8	48	6	12	24	24
v_n^B , Blanter [16]	1334	1961	-487	46	46	267	-23	-139	58	-12	-23
v_n , this work	1400	1180	-322	46	46	267	-23	-139	58	-12	-23

In the present work, the configurational interactions v_n have been estimated using a similar approach. However, in the fit to experimental values $a_C^{\gamma-gr}(c, T)$ we used for the function $\Delta G_C^{\gamma-gr}$ in (86) the interpolation of experimental data suggested by Ågren [36]:

$$\Delta G_C^{\gamma-gr} = 5550 \text{ K} - 2.31 T \quad (87)$$

rather than that used in [29], and we also varied not only v_1 but also two next constants, v_2 and v_3 . The v_n values obtained are presented in the last line of Table 1. Variations of our v_2 and v_3 with respect to their “purely deformational” values v_2^B and v_3^B lie certainly within the real accuracy of the original Blanter model as, first, this model disregards “chemical” contributions to v_2 and v_3 which can be quite notable (which is illustrated, in particular, by comparison of results of calculations of C-C interactions in ferrite based on *ab-initio* [20] and purely deformational [37] approaches [33]) and, second, it neglects both possible contributions of not-nearest Kanzaki forces [29] and a probable variation of phonon spectra with temperature (which was not measured in γ -iron but is very pronounced in the BCC iron [34, 35]). In Figs. 1 and 2 we present the carbon activity $a_C^{\gamma-gr}(x_C, T)$ and the equilibrium phase diagram ferrite-austenite calculated using the PCA expression (77) for λ with our v_n from Table 1, together with experimental data and the results of calculations based on the phenomenological model by Ågren [36].

Figure 3: Illustration of our method of estimates of saddle-point interactions Δ_n using interpolation of configurational interactions $v_n = v(R_n)$. Circles show values of v_n , and triangles, values of $\Delta_n^{(0)}$ obtained as described in the text.

Figure 4: Values of carbon-carbon interactions used in the present work. Open circles: configurational interactions $v_n = v(R_n)$; black triangles: saddle-point interactions $\Delta_n = \Delta(R_n^{sp})$. Dashed lines connect the neighboring Δ_n values to guide the eye.

Table 2. Saddle-point interactions $\Delta_n = \Delta(\mathbf{R}_n^{sp})$ (in kelvin) of carbon atoms in austenite for vectors $\mathbf{R}_n^{sp} = (\mathbf{R}'_n - \mathbf{R}_{sp})$ where \mathbf{R}_{sp} is the saddle-point position of carbon atom

n	1	2	3	4	5	6	7	8	9	10
R_n^{sp}/R_1	0.87	1.12	1.32	1.5	1.66	1.80	1.94	2.06	2.18	2.29
z_n^{sp}	4	4	8	6	4	12	8	8	12	8
Δ_n	1470	1336	1228	229	-924	-929	-543	133	133	286

n	11	12	13	14	15	16	17	18	19
R_n^{sp}/R_1	2.40	2.50	2.60	2.70	2.78	2.87	2.96	3.04	3.12
z_n^{sp}	8	14	16	4	16	16	8	20	8
Δ_n	622	564	144	-160	-310	-269	34	-43	-59

Let us now discuss the saddle-point interactions $\Delta_n = \Delta(\mathbf{R}_n^{sp})$ where $\mathbf{R}_n^{sp} = (\mathbf{R}'_n - \mathbf{R}_{sp})$, and \mathbf{R}_{sp} is the saddle-point position of carbon atom. In the second and the third lines of Table 2 we show the first 19 distances $R_n^{sp} = |\mathbf{R}_n^{sp}|$ and the coordination numbers z_n^{sp} that correspond to these \mathbf{R}_n^{sp} . To illustrate the distribution of vectors \mathbf{R}_n^{sp} in the FCC lattice, below we present the values of components of lattice vectors $\mathbf{R}'_n = (\mathbf{R}_n^{sp} + \mathbf{R}_{sp})$ (in $a/2$ units) for the first eight coordination spheres of the point $\mathbf{R}_{sp} = (0.5, 0.5, 0)$:

$$\begin{aligned}
\mathbf{R}'_1 &= (0, 1, \pm 1), (1, 0, \pm 1); & \mathbf{R}'_2 &= (0, 2, 0), (2, 0, 0), (1, \bar{1}, 0), (\bar{1}, 1, 0); \\
\mathbf{R}'_3 &= (2, 1, \pm 1), (1, 2, \pm 1), (0, \bar{1}, \pm 1), (\bar{1}, 0, \pm 1); \\
\mathbf{R}'_4 &= (2, 2, 0), (\bar{1}, \bar{1}, 0), (0, 0, \pm 2), (1, 1, \pm 2); & \mathbf{R}'_5 &= (2, \bar{1}, \pm 1), (\bar{1}, 2, \pm 1); \\
\mathbf{R}'_6 &= (0, \bar{2}, 0), (\bar{2}, 0, 0), (1, 3, 0), (3, 1, 0), (0, 2, \pm 2), (2, 0, \pm 2), (1, \bar{1}, \pm 2), (\bar{1}, 1, \pm 2); (\bar{1}, 1, \pm 3); \\
\mathbf{R}'_7 &= (0, 3, \pm 1), (3, 0, \pm 1), (\bar{2}, 1, \pm 1), (1, \bar{2}, \pm 1), (3, 0, \pm 1); \\
\mathbf{R}'_8 &= (2, \bar{2}, 0), (\bar{2}, 2, 0), (3, \bar{1}, 0), (\bar{1}, 3, 0), (0, 1, \pm 3), (\bar{1}, \bar{1}, \pm 1).
\end{aligned} \tag{88}$$

Models for estimation of the saddle-point interactions Δ_n can be constructed similarly to those for the configurational interactions v_n . The long-ranged deformational contributions to Δ_n can be calculated using the general expression for deformational interactions with the arbitrary Kanzaki forces discussed in [29], while the short-range chemical contributions can be estimated treating several first Δ_n as adjustable parameters, as it was made for the v_n . However, in this work we restrict ourselves by illustrative estimates of Δ_n based on some interpolations between v_n values in Table 1 and several simple assump-

tions. First, we assume that both the chemical and the deformational contributions to Δ_n depend only on the distance $R_n^{sp} = |\mathbf{R}_n^{sp}|$ and vary with R_n^{sp} smoothly. Second, we assume that for short distances $R_n^{sp} < R_2 = 1.41R_1$, the Δ_n values are mainly determined by the chemical contributions, while for longer $R_n^{sp} > R_2$, these values are mainly determined by the deformational contributions. Third, we assume that the dependence of the configurational interactions v_n on R_n is similar to the dependence of the saddle-point interactions Δ_n on R_n^{sp} , for both chemical and deformational contributions. Then the “chemical” interactions Δ_1 , Δ_2 and Δ_3 can be estimated using the linear interpolation between v_1 and v_2 values, as shown in Figs. 3 and 4. For the “deformational” Δ_n with $n \geq 4$ or $R_n^{sp} > R_2$, the analogous estimate of Δ_n includes the following two steps:

(A) Interpolation of dependence $v(R)$ using v_n values in Table 1, which yields “preliminary” values $\Delta_n^{(0)}$ shown in Fig. 3.

(B) Scaling of these $\Delta_n^{(0)}$ by some factor α ,

$$\Delta_n = \alpha \Delta_n^{(0)}, \quad (89)$$

with the value α determined from the fit of the diffusivity D calculated according to Eqs. (75)-(78) to the experimental data about the diffusivity of carbon in austenite.

The first step (A) is illustrated by Fig. 3. This figure shows that to obtain an adequate interpolation $v(R)$, the regions of long and “intermediate” distances R should be treated differently. At long distances $R > R_4$, we can use the simple linear interpolation between neighboring v_n values, while at $R_2 < R < R_4$, some smooth curve should be drawn between v_2 , v_3 and v_4 values. For these intermediate R , we interpolated $v(R)$ by a simple power law:

$$\begin{aligned} R_2 < R < R_3 : \quad & v(R) = C_2(R_3 - R)^m, \\ R_3 < R < R_4 : \quad & v(R) = C_4(R - R_3)^m \end{aligned} \quad (90)$$

where constants C_2 and C_4 are determined by the conditions: $v(R_2) = v_2$, $v(R_4) = v_4$. For the exponent m we tried two values, 2 and 4, and the value $m = 4$ was found to be more suitable for the fit mentioned in the point (B). The resulting interpolation $v(R)$ is shown in Fig. 3 by the dashed curve.

For the second step (B), the physical arguments in favor of the model relation (89) can be seen from the general expression for deformational interactions given by Eq. (11) in [29]. According to this expression, the deformational interaction $V_{ij}^d = V^d(\mathbf{R}_i - \mathbf{R}_j)$ between two atoms positioned at \mathbf{R}_i and \mathbf{R}_j is proportional to the integral over wave-numbers \mathbf{k} in the Brillouin zone of some expression that includes the product of two appropriate Kanzaki forces, $\mathbf{f}_{\mathbf{k}}^i$ and $\mathbf{f}_{\mathbf{k}}^j$, while each of these forces is proportional to the amplitude of displacements of neighboring host (iron) atoms due to the presence of an impurity (carbon) atom at site i or j . Therefore, for the configurational interactions v_n , the deformational contributions are proportional to the product of two Kanzaki forces, \mathbf{f}_i^{op} and \mathbf{f}_j^{op} , that describe the displacements of iron atoms induced by a carbon atom positioned in the octo-pore. At the same time, for the saddle-point interaction Δ_n , one of these factors is replaced by a Kanzaki force \mathbf{f}_i^{sp} that describes the analogous displacements of iron atoms but induced by a carbon atom in the saddle-point position, for which the carbon-iron distance $R_{\text{Fe-C}}$ is by $1/\sqrt{2}$ times smaller than that for a carbon atom in an octo-pore. Therefore, this Kanzaki force \mathbf{f}_i^{sp} can be expected to notably exceed \mathbf{f}_i^{op} . Hence the factor α in (89), which qualitatively describes the relative scale of deformational contributions to the v_n and to the Δ_n values, can notably exceed unity.

Figure 5: The diffusivity $D_C(x_C, T)$ of carbon in austenite. The symbols denote experimental values from [38] presented in [3]. The solid lines are calculated using Eq. (75) and the values v_n and Δ_n from tables 1 and 2. The dashed lines show the results of calculations by Ågren [3] based on his phenomenological model.

The description of available experimental data about the diffusivity $D_C(x_C, T)$ [38] by our model with the choice $\alpha = 2.9$ in Eq. (89) is shown in Fig. 5. This description corresponds to the following values of the saddle-point energy E_{ac} , the product $\omega_C^{eff} a^2$, and the frequency ω_C^{eff} in Eqs. (75) and (76):

$$E_{ac} = 17700 \text{ K}, \quad (91)$$

$$\omega_C^{eff} a^2 = 0.225 \text{ cm}^2/\text{sec}, \quad \omega_C^{eff} = 1.76 \cdot 10^{14} \text{ sec}^{-1} \quad (92)$$

where the value $a = 3.58 \text{ Å}$ for γ -iron [40] is used. Let us note that the choice $\alpha = 3.04$ in Eq. (89) would yield the values of $D_C(x_C, T)$ which virtually coincide with those obtained by Ågren [3]. However, the choice $\alpha = 2.9$ seems to better describe the low-temperature data by Wells et al. [38] which agree with those obtained by Smith [39]. The saddle-point interactions Δ_n which correspond to $\alpha = 2.9$ are presented in Table 2 and Fig. 4.

Both experimental and theoretical results presented in Fig. 5 show that the diffusivity D_C sharply rises with increase of the carbon concentration x_C . In accordance with Eqs. (10), (11), (75) and (78), it seems to indicate on the presence of a significant attraction in the saddle-point interactions Δ_n , as this attraction lowers the saddle-point energy E_C^{SP} for the inter-site jumps of carbon atoms. In the model estimates of interactions shown in Fig. 4, it corresponds to the presence of significant negative Δ_n at “intermediate” carbon-carbon distances R lying in the interval $1.6R_1 \lesssim R \lesssim 2R_1$. The rise $D_C(c, T)$ with x_C mentioned above can imply that such significant attraction is present not only in our model estimates, but also in the real saddle-point interactions of carbon atoms in austenite.

Let us now discuss the values of the pre-factor ω_C^{eff} and the “transition state entropy” ΔS_C^{SP} in (8) which correspond to the estimate (92). The attempt frequency ω_{pv} in (8) for our case can be estimated as the frequency ω_C^γ of local vibrations of carbon in austenite. These vibrations have been experimentally studied by Sumin et al. [41] who found:

$$\omega_C^\gamma \simeq 75 \text{ meV} = 1.14 \cdot 10^{14} \text{ sec}^{-1}. \quad (93)$$

Note that this ω_C^γ exceeds the Debye frequency of γ -iron, $\omega_D^\gamma = 0.43 \cdot 10^{14} \text{ sec}^{-1}$ [42], by about three times. Then using Eq. (8) with $\omega_{pv} = \omega_C^\gamma$ and $\omega_{pv}^{eff} = \omega_C^{eff}$ from (92), we obtain:

$$\Delta S_C^{SP} \simeq 0.4, \quad \bar{\omega}_C^{sp} \simeq 0.9 \omega_C^\gamma. \quad (94)$$

These relations show that the “softening” of saddle-point frequencies ω_C^{sp} with respect to ω_C^γ for carbon in austenite is rather weak (if any), unlike Fe-Cu substitution alloys discussed in Sec. 2.1, while the saddle-point entropy ΔS_C^{SP} is by an order of magnitude lower than the analogous ΔS_{Cu}^{SP} and ΔS_{Fe}^{SP} values for the Fe-Cu alloys (as estimated by SF [14]). The difference can be related (at least, partly) to the above-mentioned inequality $\omega_C^\gamma \gg \omega_D^\gamma$ which implies that the dynamics of carbon atoms in austenite is much faster than the iron atom dynamics. In such conditions, an assumption of “a local thermodynamic equilibrium” for the saddle-point transition state, as well as the entropy notion for this state can be not fully adequate and should be used with some caution.

Note that Eqs. (94) correspond to the pre-factor ω_C^{eff} of the factor γ in (76) which determines the diffusivity (75) in the dilute alloy limit. Therefore, these equations have no

relevance to the illustrative estimates of carbon-carbon interactions discussed above, but they provide some definite information about the microscopic characteristics of diffusion of carbon in γ -iron.

Finally, let us compare the microscopic description of thermodynamic and diffusional characteristics of carbon in austenite presented in this work to their phenomenological description developed by Ågren [2, 3, 36]. Both approaches use a similar number of adjustable parameters, and the quality of agreement between the results obtained and the experimental data shown in Figs. 1, 2 and 5 is similar. However, the microscopic approach seems to provide a more adequate physical understanding of the phenomena considered. It also opens possibilities for developments of fully first-principle descriptions with no adjustable parameters, as demonstrated by SF [14] for Fe-Cu alloys. In addition to that, the microscopic expression (75) for the diffusivity seems to elucidate a number of principal points not discussed earlier. First, it shows that the diffusivity can be written in the form of the product of “thermodynamic” and “kinetic” (or “saddle-point”) factors, and the thermodynamic factors include not only the so-called Darken-factor $\partial \ln a_X / \partial \ln c$ usually written [2], but the concentration derivative of the activity itself, $\partial a_X / \partial c$. Second, the microscopic relations (75)-(78) enable us to estimate the “transition state entropy” ΔS^{SP} from experimental data, as was demonstrated for carbon in austenite. Third, these microscopic relations allow to relate the concentration dependence of the activity a_X and the diffusivity D_X to both the configurational and the saddle-point interactions between interstitial atoms X, in particular, between carbon atoms in austenite. Therefore, the analysis of experimental data about $a_C(x_C, T)$ and $D_C(x_C, T)$ enables us to get an idea about the type and the scale of these interactions.

5 CONCLUSIONS

Let us summarize the main results of this work. The fundamental master equation for the probability of various atomic distributions in an alloy is used to derive the basic equations of diffusional kinetics in alloys. The microscopic parameters entering these equations can be calculated by *ab-initio* methods, as was demonstrated by SF for iron-copper alloys [14], or using various theoretical models. For substitution alloys, the diffusional transformation kinetics is described by the “quasi-equilibrium” kinetic equation (QKE) derived in Sec. 2.1. This equation (28) generalizes its earlier version presented in [15] by taking into account possible “interaction renormalization” effects which can be important for the vacancy-mediated kinetics [11, 13]. In sec. 2.2 we describe the calculations of local chemical potentials λ_i and correlators b_{ij} entering the QKE (28) with the use of some analytical methods which combine simplicity of calculations with a high accuracy, particularly for dilute alloys. In Sec. 2.3 we reduce the QKE (28) describing the vacancy-mediated kinetics to the kinetic equation for some equivalent direct-atomic-exchange model which is suitable for computer simulations.

The microscopic equations describing diffusion of interstitial atoms X in an interstitial alloy Me-X are derived in Sec. 3. These equations have a simple form (65) or (68), which enable us to obtain the explicit analytical expressions for the diffusivity $D = D_X$. These expressions for D given by Eqs. (71) or (75) have a simple form of products of three factors: the concentration derivative of the thermodynamic activity a_X of atoms X; the correlator b_X given by Eqs. (67) or (78) which describes the influence of interactions between atoms X on the activation barrier for the inter-site jumps of atoms X; and the concentration-independent factor γ describing the diffusivity in the dilute alloy limit. This

microscopic expression for D differs notably from those used in phenomenological treatments [1]-[4], in particular, by the presence of the concentration derivative $\partial a_X/\partial c$ rather than the so-called “Darken-factor” $\partial \ln a_X/\partial \ln c$ usually written. We also derive equations describing diffusion of interstitial atoms X in a multicomponent alloy (Me₁Me₂...)-X.

In Sec. 4 we apply the results of Sec. 3 to microscopically treat the problem of diffusion of carbon in austenite discussed by a number of authors [1, 2, 3, 4]. Our treatment is based on the microscopic model of C-C interactions in austenite suggested by Blanter [16] which supposes a strong “chemical” repulsion at short C-C distances R and a purely deformational interaction at longer R . To estimate the configurational interactions $v(R)$ which determine the carbon activity a_C , and the “saddle-point” interactions $\Delta(R)$ which determine the above-mentioned correlator $b_X=b_C$, we use some plausible assumptions about the dependences $v(R)$ and $\Delta(R)$ which include adjustable parameters. The interaction models obtained enable us to describe both the thermodynamic and the diffusional properties of carbon in austenite at the same level of accuracy as that achieved in phenomenological treatments [1, 2, 3, 4, 36]. At the same time, the microscopic approach used enables us to make a number of qualitative conclusions about the carbon-carbon interactions and the characteristics of diffusion of carbon in austenite, in particular, about the presence of a significant C-C attraction at intermediate R and about a rather low value of the “transition state entropy” ΔS_C^{SP} given by estimate (94).

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